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CHEMICALLY DERIVATIZED SEMICONDUCTOR PHOTOELECTRODES
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"CHEMICALLY DERIVATIZED SEMICONDUCTOR PHOTOELECTRODES"

by

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Prepared for publication in the Journal of Chemical Education

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CHEMICALLY DERIVATIZED SEMICONDUCTOR PHOTOELECTRODES

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Abstract:

Semiconductor-based photoelectrochemical cells are the best man-contrived devices for the direct conversion of sunlight to electrical or chemical energy using chemically-based systems. Deliberate modification of the surface of the semiconductor photoelectrode is useful in improving the rate of desired processes and in suppressing undesirable anodic corrosion associated with photoanodes. Illustrations of the use of surface modification will be presented with specific examples coming from work with molecular-based derivatizing reagents and from the use of metals or metal oxides coated onto the photoelectrode surface.

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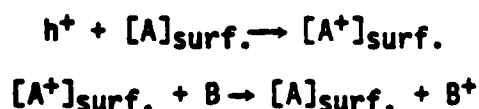
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Semiconductor-based photoelectrochemical cells are now known to be capable of effecting the sustained conversion of solar energy to electricity or to chemical fuel in the form of redox products.¹⁻³ Not surprisingly, it has been concluded that the properties of the surface of the semiconductor photoelectrode in contact with the electrolyte solution govern the performance of these energy conversion devices. The key characteristics of photoelectrode durability, output photovoltage, and output photocurrent can be favorably altered by modification of the surface of the semiconductor photoelectrode.⁴ The aim of this article is to highlight the significant results from modification of photoelectrode surfaces.

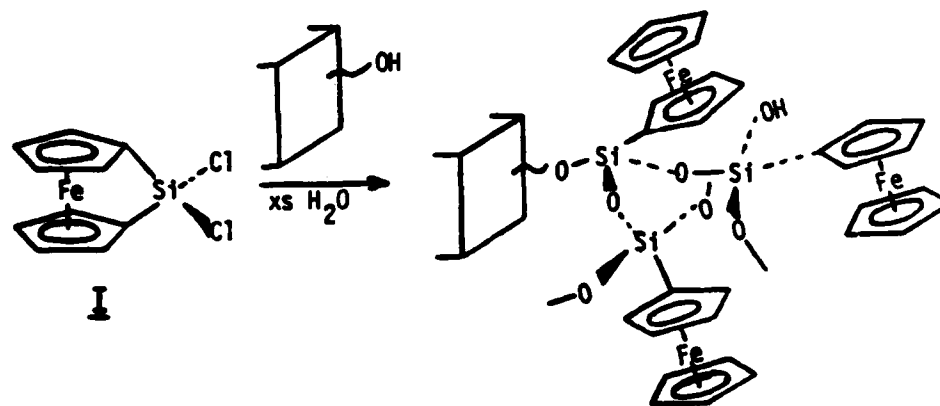
Suppression of Photocorrosion of n-Type Semiconductors. It is well-known that an n-type semiconductor can undergo decomposition when used as a photoanode in an electrochemical cell.⁵⁻⁷ Clearly, if an n-type semiconductor is to be used for the sustained conversion of light to chemical or electrical energy in a photoelectrochemical cell, the photoanodic decomposition of the electrode must be suppressed. It is also known that there are desirable interfacial redox reactions that can successfully compete with the photoanodic decomposition of the electrode.¹ For example, the oxidation of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ can compete with the photooxidation of n-type Si in non-aqueous solutions.⁸ The point is that while all n-type semiconductors are thermodynamically unstable when illuminated with $>$ band gap light, reductants can kinetically compete for the photogenerated oxidizing equivalents (holes, h^+) that are available at the surface of the semiconductor. Thus, the ability to sustain a desired photoanodic process can be viewed as a kinetic competition between two thermodynamically favorable processes. Thermodynamics defines the realm of possibility, but kinetics can fortunately be manipulated to realize a desired objective.

When a reductant A is found to suppress the photoanodic corrosion of an n-type semiconductor electrode it may or may not be easy to find other reagents that will also be successful in competing for the photogenerated h^+ . It is sometimes the case that the desired reaction is $B \rightarrow B^+$. This may be a process that does not effectively compete with the photoanode decomposition, owing to poor kinetics for the $h^+ + B \rightarrow B^+$ process compared to the decomposition involving the photogenerated h^+ . In such a case it may be possible to modify the surface of the semiconductor with a derivative of A in order to suppress the corrosion of the photoelectrode while preserving the ability to oxidize B:



The role of the surface-confined A, $[A]_{\text{surf.}}$, is to capture the photogenerated oxidizing equivalent to preclude the anodic corrosion of the semiconductor, forming $[A^+]_{\text{surf.}}$. The solution species B can be oxidized to B^+ by $[A^+]_{\text{surf.}}$ in a heterogeneous reaction regenerating $[A]_{\text{surf.}}$ in the process. Thus, whether the oxidation of B can be effected depends on the oxidizing power of $[A^+]_{\text{surf.}}$ and the kinetics for its reaction with B. In many instances the redox properties of the surface-confined redox system and its solution analogue are very similar.⁹ It can be concluded, therefore, that an n-type semiconductor functionalized with the $[A^+/A]_{\text{surf.}}$ system should be capable of effecting the sustained photooxidation of B if the A^+/A system in solution is capable of both suppressing the photodecomposition of the anode and oxidizing B. The main advantage is that the modified n-type semiconductor should be useful in effecting many desirable redox processes, not just the oxidation of A.

The functionalization of semiconductor surfaces can be brought about in many ways.⁴ Consider the example cited above of n-type Si made durable by the addition of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ to a non-aqueous solution.⁸ A derivative of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$, I, is a reagent that can react with surface-OH groups and trace amounts of H_2O to yield more than monolayer quantities of the ferrocene-based redox material covalently anchored to a surface:



It has been demonstrated that n-type Si electrodes derivatized in this way can be used to sustain the photooxidation of B for any B oxidizable with the solution species $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2^+$, the oxidized form of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$.^{10,11} In this system the $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ is the reductant A of the foregoing paragraph. The additional finding is that the surface-confined material derived from I also allows the use of n-type Si photoanodes in aqueous electrolytes where the photoanodic formation of SiO_x is most severe and where the $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ itself is not useful owing to its insolubility. The surface-confined reagent, however, is useful and allows the use of n-type Si photoanodes for many other reactions other than the oxidation of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ in non-aqueous solvents.

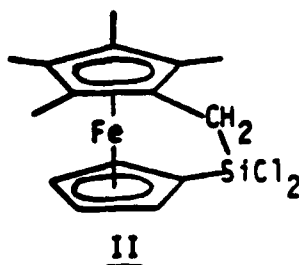
Unfortunately, the surface-confined material derived from I is not useful in effecting the oxidation of H_2O at an n-type Si photoanode. The oxidizing power of the $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2^+$ is not sufficient to oxidize H_2O . Further, it is unlikely that simple one-electron redox reagents would have good kinetics for

the four-electron oxidation of H_2O to form O_2 . Another approach to electrode modification has yielded some success in this regard, however. The surface of n-type Si can be modified by the deposition of Pt followed by a heat treatment to yield a platinum silicide surface. Electrodes treated in this way can be durable with respect to anodic corrosion in aqueous electrolyte solutions for the oxidation of halides to form halogens.¹² Further modification with RuO_x yields a surface from which evolution of O_2 from H_2O oxidation can be detected upon excitation with light absorbed by the n-type Si. The platinum silicide protective coating differs from the coating derived from reagent I in that it has electronic conductivity whereas h^+ movement through the film from I can only occur through a sequence of electron transfer processes involving the individual ferrocene-based redox centers. A faster movement of h^+ through the metallic overcoat can be expected, but the surface derived from treatment with reagent I has molecular properties that may allow unique chemical reactions to be effected. The fast h^+ movement and a surface having exposed molecular species can both be realized by functionalizing the photoanode surface with polypyrrole, an electronically conducting polymer formed by the anodic polymerization of pyrrole.¹³⁻¹⁶

Improvement of Rate of a Desired Anodic Process. In many cases an n-type semiconductor can be made more durable by surface modification. However, it is not always true that the modification used to bring about durability allows the redox event of interest to be observed with high efficiency. When electrode decomposition is not occurring and the desired redox event is not fast, recombination of the photoexcited electron and the photogenerated hole can occur. This means that the optical excitation is degraded into heat or emitted as lower energy optical radiation. When there is a thermodynamically possible process that occurs slowly catalysts may be useful in improving the

rate. One example has already been mentioned, namely the case of n-type Si made durable by the platinum silicide but which does not yield efficient oxidation of H_2O . The rate of oxidizing H_2O can be improved by the deposition of the RuO_x , known to be a good surface from which to evolve O_2 .¹² More recently, the efficiency for Cl_2 generation from the photooxidation of Cl^- at illuminated n-type MS_2 ($M = Mo, W$) has been significantly improved by the deposition of a catalytic amount of Pt onto the MS_2 electrode surface.¹⁷

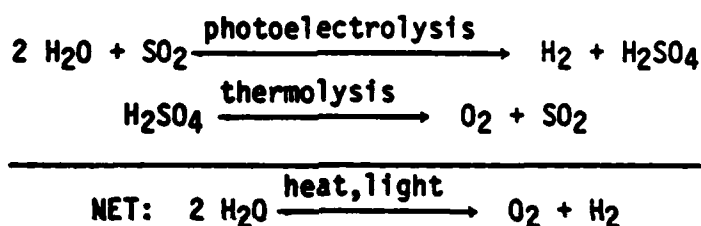
The examples of rate improvement cited in the paragraph above do not involve the use of molecules as the catalytically active species. Rather, the catalyst is one which can be useful in bringing about oxidations that involve more than one oxidizing equivalent per product molecule. In some cases the catalysis may be best brought about using a molecular entity. One such example involves the oxidation of large biological molecules such as horseheart cytochrome c, cyt c, that do not rapidly exchange electrons with electrodes for a variety of reasons. However, small redox molecules do readily exchange electrons with large biological molecules and are used as redox "mediators".¹⁸ Thus, surface-confined mediators should be useful in improving the rate of photooxidation at illuminated n-type semiconductor electrodes. Recent studies of n-type Si derivatized with reagent II establish that photooxidation of the



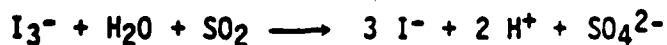
reduced form of cyt c can be effected at the modified surface.¹⁹ The reaction is not doable at the "naked" photoanode because the kinetics are poor and the decomposition of the photoanode is severe. Improving the durability of the

n-type Si by using a procedure such as the platinum silicide is not likely to be successful, since the problems that plague biological redox molecules will emerge at the platinum silicide surface exposed to the electrolyte solution. The ability to effect the efficient photooxidation of biological substances may ultimately be useful in oxidizing H₂O, since O₂ evolution from H₂O oxidation occurs in the natural photosynthetic system.

Catalysis of the oxidation of SO₂ to SO₄²⁻ in strong acid solution²⁰ provides a final example of surface modification of interest in connection with semiconductor photoanodes. Interest in this system stems from the prospect that a hybrid scheme for water splitting can be envisioned:



The photooxidation of SO₂ to SO₄²⁻ can be effected in strong acid solution at illuminated n-type MS₂ electrodes. The key is that the solution must contain a small amount of the I₃⁻/I⁻ redox couple. The I₃⁻/I⁻ system specifically adsorbs onto the MS₂ to bring about a favorable set of interface energetics. The adsorption of the I₃⁻/I⁻, though, is not irreversible as in the covalent attachment of reagents I and II. Rather, the adsorption of the I₃⁻/I⁻ is rapidly reversible. Nonetheless the interaction of the MS₂ with the I₃⁻/I⁻ couple is sufficiently strong to bring about a favorable change in the interface energetics for the SO₂ oxidation. Further, the primary photo-oxidation product, I₃⁻, from the oxidation of I⁻ can rapidly oxidize the SO₂:

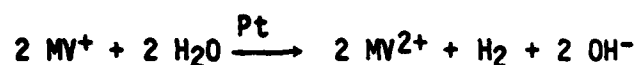


Thus, in the photoelectrolysis of $\text{H}_2\text{O}/\text{SO}_2$ in acid solution the I_3^-/I^- plays two roles: the strong interaction with the MS_2 surface brings about a change in interface energetics that improves the output photovoltage and the redox chemistry of the adsorbed I_3^-/I^- system brings about an improvement in the rate of the SO_2 oxidation. The n-type WS_2 based cell for the photoelectrolysis of $\text{H}_2\text{O}/\text{SO}_2$ represents one of the most efficient energy conversion devices for the direct generation of energy-rich materials where visible light is the only energy input.²⁰ Further, the surface modification in situ by the I_3^-/I^- redox couple exploits the surface chemistry of the MS_2 ; the favorable change in interface energetics by adsorption of the mediator system is not common occurrence.

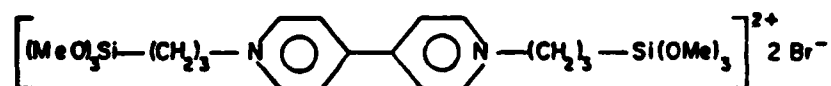
Improvement of Rate of a Desired Cathodic Process. Photocathodic processes can be efficiently effected at p-type semiconductors where the photoexcited electron, e^- , not the oxidizing h^+ , comes to the surface of the electrode available for some redox event. The problem of anodic decomposition of p-type semiconductors is often nonexistent, perhaps because the reducing equivalents at the surface protect the surface from oxidative decomposition. Generally, the redox process that has been the object of most attention, namely H_2 formation, does not occur with good kinetics at many electrodes.²¹ Semiconductors are unexceptional in that they do not have good kinetics for H_2 evolution.²² Thus, catalysis of H_2 evolution is desirable. Surface modification has proven to be useful in significantly improving the efficiency for the photocathodic evolution of H_2 from H_2O via catalysis of the reduction process.

One approach to catalyzing the evolution of H_2 emerged from the demonstration that kinetics, not energetics, for the process are the limiting factor.²² The result that demonstrates that the kinetics are limiting comes from the comparison of the efficiency for reducing N,N'-dimethyl-4,4'-bipyri-

dinium, MV^{2+} , versus H_2O at a pH where MV^{2+} and H_2O are equally difficult to reduce in thermodynamic terms. Nearly zero efficiency is obtained for the reduction of H_2O , whereas good efficiency can be obtained for the reduction of MV^{2+} at illuminated p-type semiconductors such as Si, InP, and GaAs.²² The reduction of MV^{2+} to form MV^+ is known to occur with good kinetics at many electrode surfaces and again the semiconductors are unexceptional. The important conclusion is that a reducing reagent, MV^+ , that is just as potent a reductant as H_2 can be produced at an illuminated p-type semiconductor with good efficiency. Further, it is known that the $MV^{2+}/^+$ system can be equilibrated with the H_2O/H_2 via Pt catalysis:



Thus, derivatization of p-type Si electrode surfaces with the N,N'-dialkyl-4,4'-bipyridinium reagent, III, followed by deposition of a noble



III

metal such as Pt or Pd results in an efficient photocathode.²³ Like reagents I and II, reagent III has hydrolytically unstable functionality that allows it to react with surface-OH groups and with H_2O to bring about the attachment of greater than monolayer quantities of the redox centers. The 2+ charge on the monomer units can be useful in incorporating the Pt or Pd precursor inasmuch as metal complex anions such as $PtCl_4^{2-}$ can be electrostatically bound and subsequently reduced to the active zero valent Pt. The incorporation of the Pt or Pd is essential to efficient H_2 generation, since the reduced form of

the surface-confined material from III does not have good kinetics for reaction with H_2O to produce H_2 . The Pt or Pd equilibrates rapidly with both the surface-confined redox material and with the H_2O/H_2 . Long term durability of surface-confined catalysts remains an important concern, but the success realized so far is encouraging.

It is also possible to significantly improve the kinetics for the photo-reduction of H_2O by the deposition of Pt onto the surface of the semiconductor in a manner similar to that in improving the efficiency for Cl_2 formation at the illuminated n-type MS_2 .²⁴ However, direct deposition of Pt onto p-type semiconductors has the tendency to form an ohmic contact with the semiconductor that can completely remove the photovoltage.²⁵ The use of the redox polymer can prevent the semiconductor surface from being contacted by the Pt, precluding reduction in the output photovoltage. In principle, any mechanism to bring about the catalysis that does not alter overall energetics (as happens in the I_3^-/I^- case described above) will give the same theoretical efficiency. Whatever the procedure, it is clear that modification of the surface of a photocathode can significantly improve the efficiency for production of H_2 .

The molecular properties of the surface-confined material derived from III can also be exploited. The photoreduction of the oxidized form of cyt c can be effected at a p-type Si electrode functionalized with III, whereas the reduction cannot be detected at the naked electrode even though it is durable in aqueous solution.²⁵ Interestingly, the $MV^{2+}/+$ system is a good mediator for biological redox reagents that are known to be able to catalyze the reduction of H_2O to produce H_2 , the reduction of N_2 giving NH_3 , and the reduction of CO_2 to produce $HCOOH$. None of these processes has good kinetics at the naked p-type semiconductor photocathodes, and yet all of these would be

significant targets for practical solar conversion systems.

CONCLUSIONS

The deliberate modification of semiconductor photoelectrodes to improve durability and to enhance the rate of desirable interfacial redox processes has been summarized for a variety of systems. Modification with molecular-based systems or with metals or metal oxides has yielded results that signal an important role for surface modification in devices for fundamental study and in practical energy conversion. A question that arises is: Are there any direct solar fuel producing systems that will not require modification and redox catalysis at interfaces?

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